Studies on Thermal Behaviours of Naphthalene Based Vinyl Ester Resins: Synthesis and Characterization

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Abstract

The present article deals with the preparation of vinyl ester resins from synthesized epoxy with unsaturated acrylate in presence of catalyst and controlled inhibitor. In this synthesis, the raw material of the epoxy resin 2, 6-dimethylol-4-methylphenol-naphthol was tagged with methyl acrylate / ethyl acrylate; resultant the epoxy resin in form of vinyl ester resin was synthesized. FT-IR and ^{1}H-NMR were used to evaluate the structures of resulting vinyl ester resins. Thermal characterizations of resultant resins were monitored by differential scanning calorimeter (DSC) using curing agent and thermo gravimetric analysis (TGA).

Keyword: Epoxy Resin, Methyl Acrylate, Ethyl Acrylate, TGA, FTIR Method.

Introduction

Vinyl ester resins classified as thermosetting polymers, are employed for obtaining high performance composites and also find in various industrial applications such as surface coatings, adhesives, printed circuit board coatings, ultraviolet cured inks, for instance laminates and composites, tooling, molding, casting and fibre reinforced plastics [1-2].

These resins have superior heat resistance, excellent mechanical and chemical properties as compared with other thermosetting resins such as unsaturated polyester resins. Commercial polymers which comprise fibres, films, laminates and plastics, etc., have one major limitation that have low melting point, hence they cannot operate at high temperatures. They readily oxidise or decompose at below 250^0C. Several interesting solutions have been proposed to make such polymers which retain useful properties at 300^0C or much higher temperatures. These polymers should possess high temperature resistance properties over long periods. These high temperature polymers are used to make aerospace adhesives [3-5]. Recent trend in polymer research point to an increasing demand for the development of high temperature polymer in various industrial applications such as in electrical insulation, protective coatings and for various kind of films and plastics, etc. Most of the studied related to the synthesis of vinyl ester resins derived from diglycidyl ether of bisphenol-A reported [6-8]. The present article comprises synthesis, characterization and thermal properties of vinyl ester resins based on alkyl substituted epoxy segments.

Experimental Work

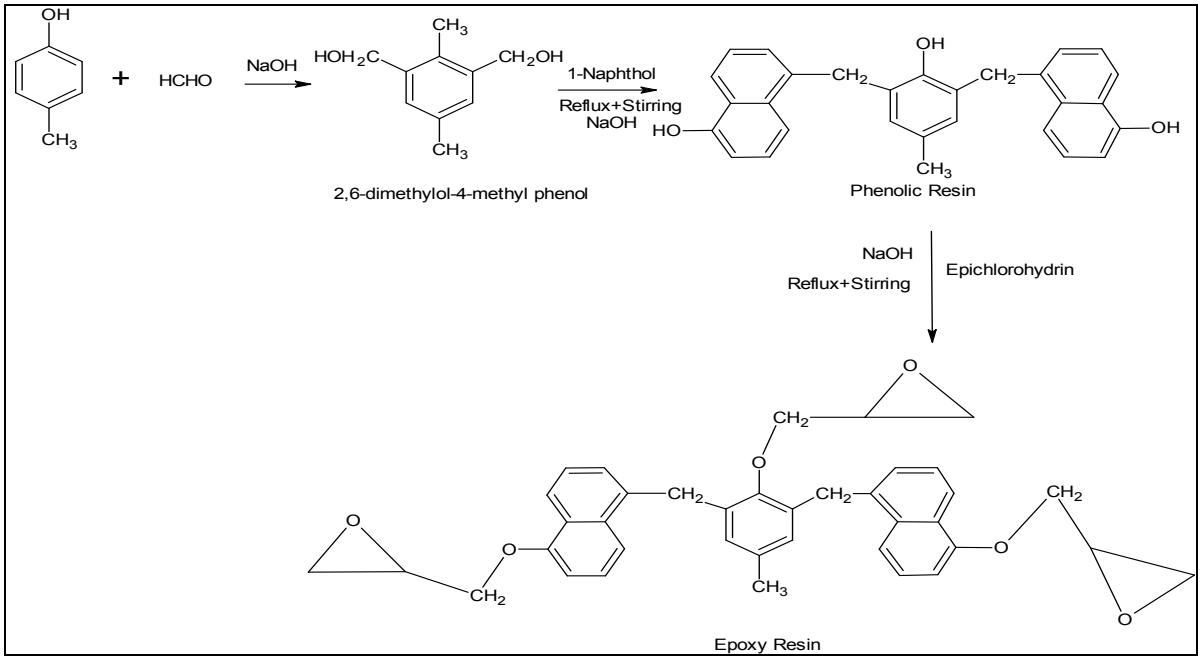
Materials

4-methylphenol, formaldehyde, 1-naphthol, epichlorohydrin and NaOH pellets were used for the preparation of epoxy resin. Methyl acrylate, ethyl acrylate, triethylamine and hydroquinone were used for the synthesis of vinyl ester resin.

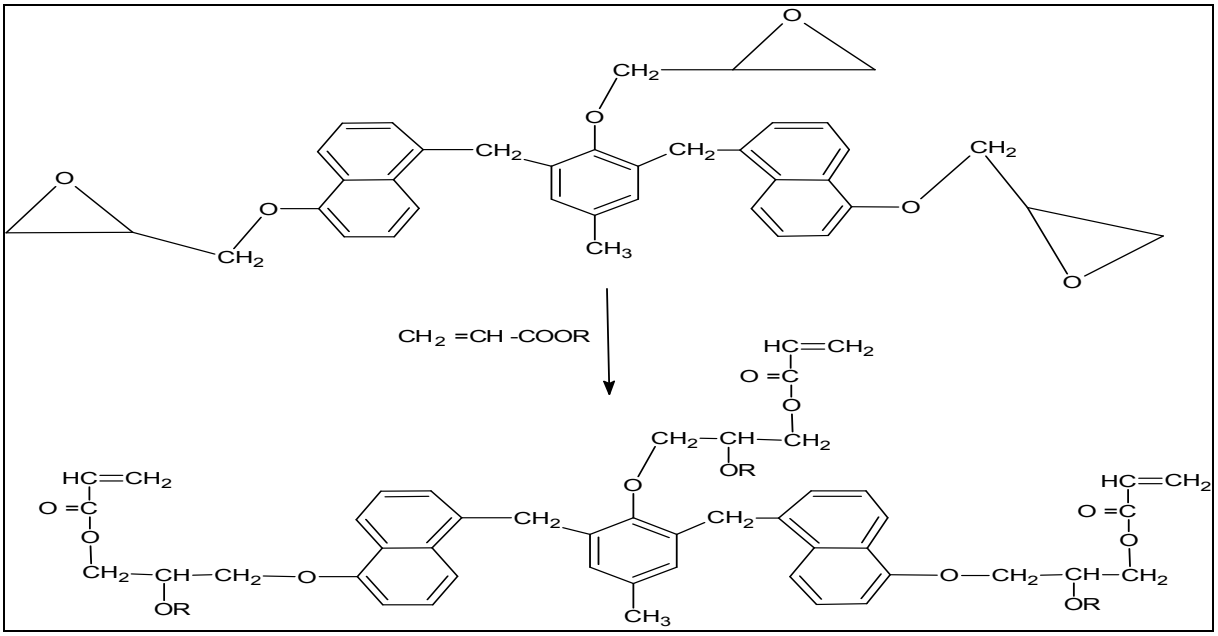
Synthesis of epoxy resin

The epoxy resin was prepared by a simple condensation reaction. The resin was prepared by using method reported [(5)]. The general procedure for the synthesis of epoxy resin is as follows.

In three necked flask equipped with a mechanical stirrer and a condenser 4-methylphenol and formaldehyde in 1:2 ratios were charged in basic medium using NaOH. The solution was heated to 70°C-80°C with constant stirring to form dimethylol resin. Phenolic resin was prepared by the reaction of the above prepared resin with 1-naphthol for 16 hours at 90°C. Epoxidation of phenolic resin was done with epichlorohydrin to form triglycidyl ether in presence of NaOH for 8-10 hours. The reaction scheme for the synthesis of epoxy resin is shown in Scheme 1.



Scheme 1: Reaction pathway for the synthesis of epoxy resin



R= -CH_3, -C_2H_5 **Scheme 2: Reaction pathway for the synthesis of VER resin**

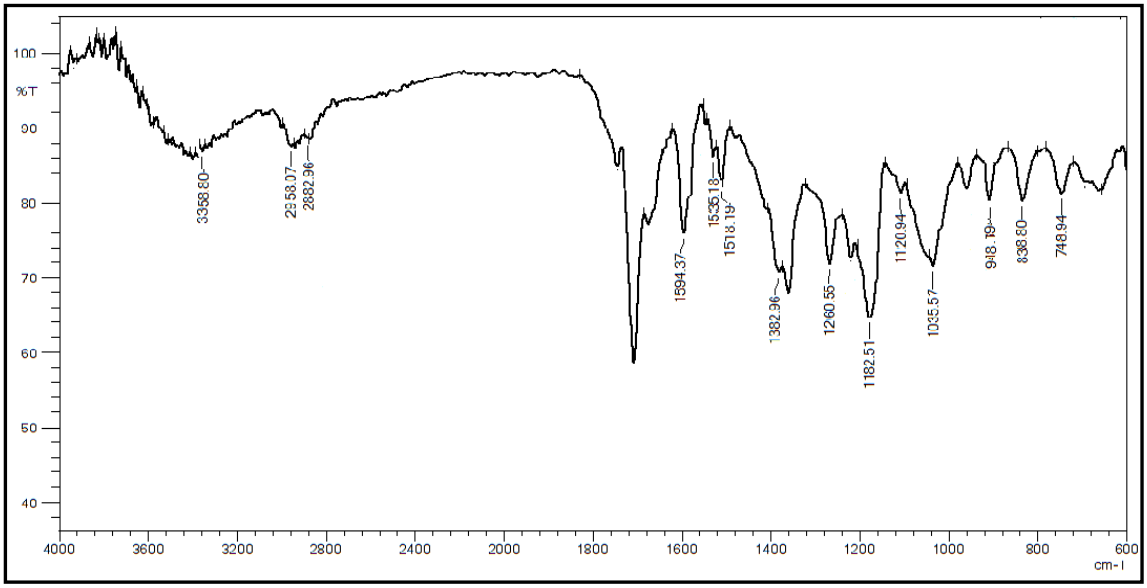
Synthesis of vinyl ester resin

The epoxy resin and methyl acrylate/ethyl acrylate were charged in three necked flask equipped with a mechanical stirrer. The reaction mixture was heated at 90^{o}C -100^{o}C in presence of triethylamine (1 percent of total weight of epoxy resin) as a base catalyst. To this 0.03% of hydroquinone was added as an inhibitor. The estrification reaction was carried out for 6 hours to obtain resin. The synthesized resin was cooled and dissolved in toluene and filtered using whatman filter paper to remove salt. Toluene was distilled off under reduce pressure. The product was dried in the oven at 60^{o}C for duration of 48 hours. Vinyl ester was formed in viscous form of brown coloured liquid resin which soluble in organic solvent such as acetone, ether, benzene etc. The reaction scheme for the synthesis of vinyl ester resin is shown in Scheme 2.

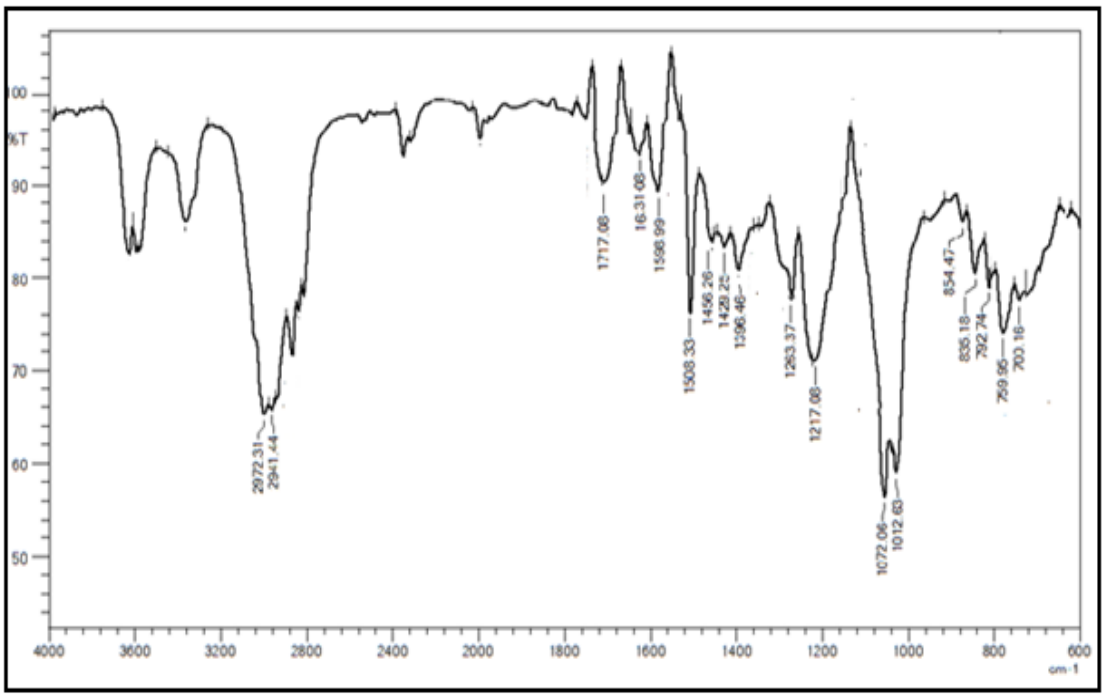
Result and discussion:

The structural characterization of epoxy resin and vinyl ester resin was done using FT-IR spectroscopy. The FT-IR of the sample was recorded on a Perkin Elmer FT-IR spectrophotometer, using the potassium bromide pellet method. The pellet of resin sample was prepared from a mixture of 60 mg potassium bromide and 1 mg of resin sample. The structural characterization of vinyl ester resin was also done using ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of these resin samples were recorded on a Bruker Avancen II 400 NMR spectrometer. $CDCl_3$ was used as a solvent and ^{1}H chemical shifts were measured with respect to tetramethylsilane (TMS) which used as an internal standard.

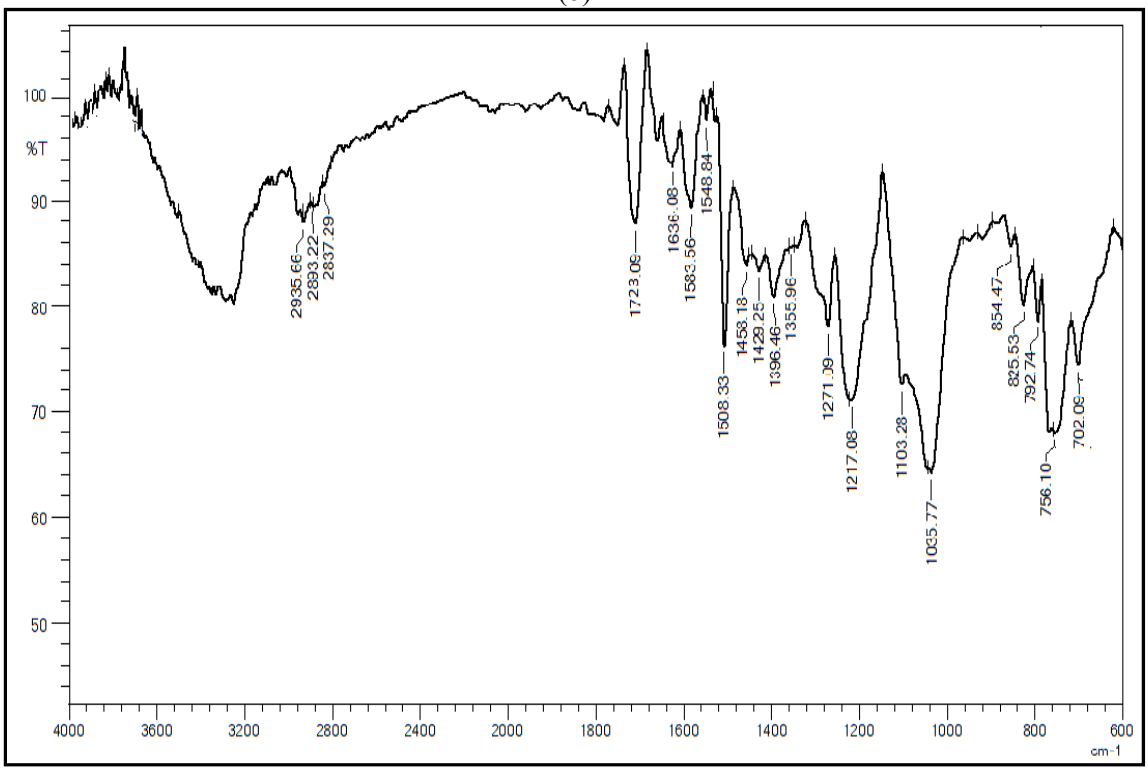
FT-IR spectra of epoxy and vinyl ester resin are shown in figure-1. As it can be observed the characteristic absorption band due to the oxirane ring at 918 cm^{-1} (figure-1a) is replaced by a band at 1717 cm^{-1} and 1723 cm^{-1} in vinyl ester spectrum figure-1b and figure-1c respectively, due to carbonyl groups in methyl and ethyl acrylate ester of vinyl ester resins. Another absorption peaks at 1631 cm^{-1} and 1636 cm^{-1} in vinyl ester spectrum were due to the stretching vibrations of the acrylol double bond in the acrylate which confirms the formation of vinyl ester.^{1}H-NMR spectra of vinyl ester resins (figure-2) shows the chemical shift of aromatic protons in the range of 6.9-7.8 ppm. Vinylic protons of methyl and ethyl acrylate show the signal in the region of 5.8 to 6.4 ppm. The resonance signals of the methylene protons were observed at 3.4- 4.6 ppm.



(a)

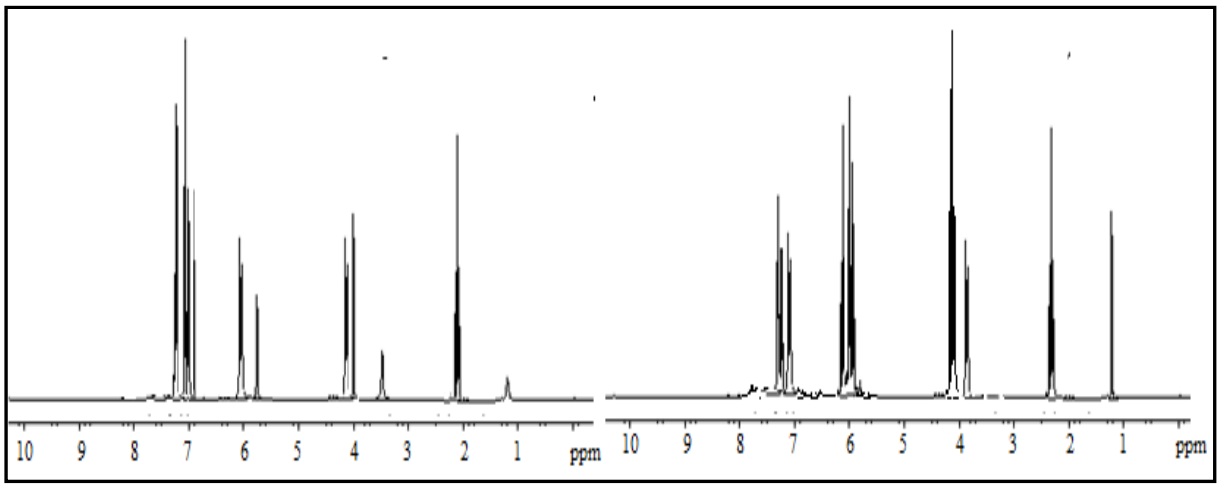


(b)



(c)

Figure 1. FT-IR Spectra of (a) Epoxy resin; (b) Vinyl ester resin of methyl phenol with methyl acrylate (VER I); and (c) Vinyl ester resin of methyl phenol with ethyl acrylate (VER II)



(a) (b)

Figure 2. ^{1}H-NMR Spectra of (a) VER I; and (b) VER II

Thermal Studies:

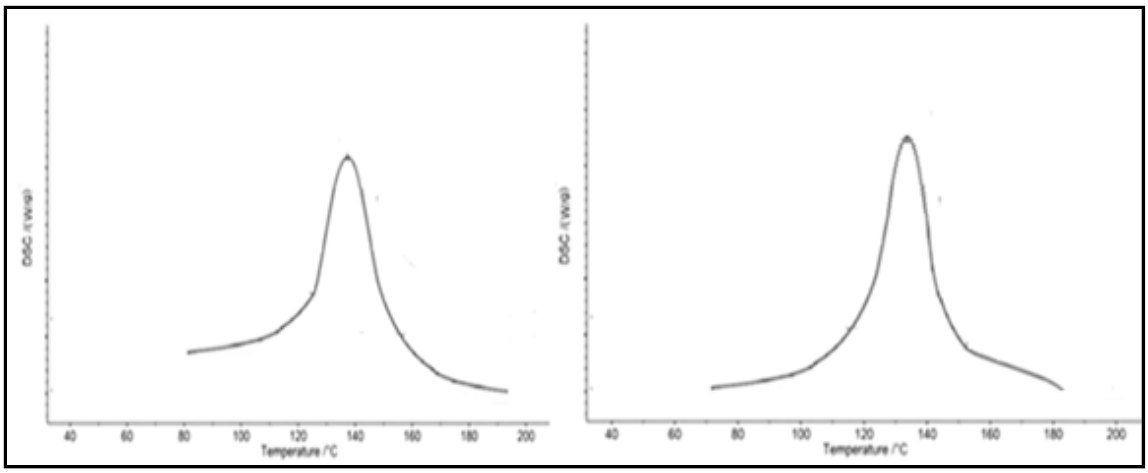
Curing of all these vinyl ester resins was done on a Universal VG03 differential scanning calorimeter (DSC) with benzoyl peroxide used as a catalyst at heating rate of 10°C/min. DSC data of all the samples are furnished in Table 1 revealed that cured samples give a single exothermic peak shown as Figure 3. The samples of vinyl ester resins were also analyzed by thermo gravimetric analysis (TGA) on Du Pont 950 thermogravimetric analyzer at a heating rate of 10 K min^{-1}. The results indicate that the degradation of samples occurs at about 150°C and their initial weight loss is about 2%-3%. The rate of degradation increased very rapidly between 300°C to 450°C and the product was lost completely beyond 600°C as shown in Figure 4. The TGA data of resultant resins are shown in Table 2**.** It is apparent that the thermal stability of VER II was better as compared to VER I.

Table-1: DSC Curing data of Vinyl Ester Resins

Comp.	Curing Temperature °C		
	Initial Temp. (T_i)	Peak Temp. (T_p)	Final Temp. (T_f)
VER I	122	133	145
VER II	128	139	151

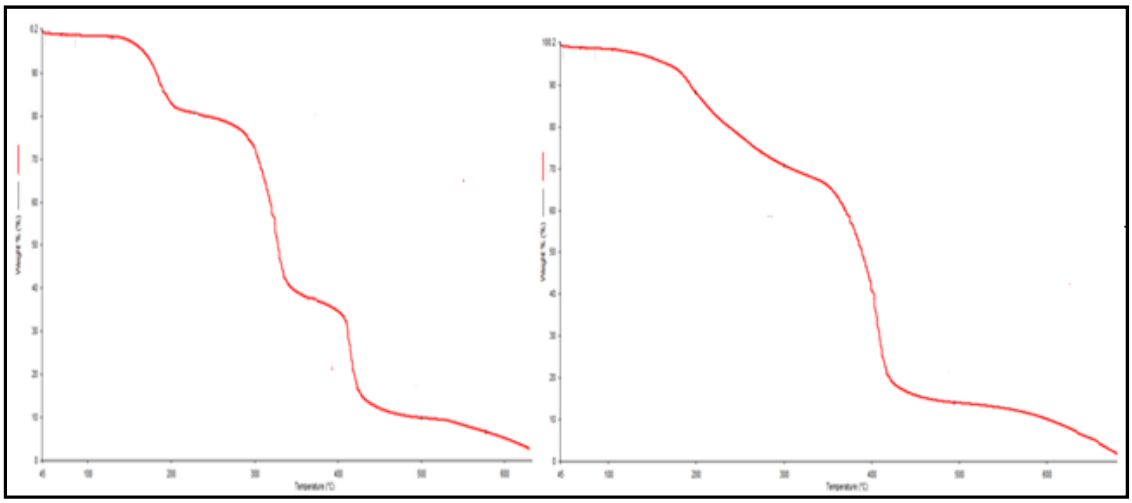
Table-2: TGA data of Vinyl Ester Resins

Comp.	% Wt. loss at various temperatures					
	150°C	200°C	300°C	400°C	500°C	600°C
VER I	2.24	18.94	29.45	65.17	90.80	94.23
VER II	2.05	11.94	29.21	59.06	87.15	90.25



(a) (b)

Figure 3: DSC spectrum of Vinyl Ester Resins (a) VER I; and (b) VER II



(a) (b)

Figure 4: TGA spectrum of Vinyl Ester Resins (a) VER I; and (b) VER II

Conclusion

In this work, various types of vinyl ester resin samples VER I and II were synthesized by the estrification of epoxy resin based on 2, 6- dimethylol-4-methylnaphthol with methyl acrylate and ethyl acrylate in presence of triethylamine as catalyst and hydroquinone as inhibitor. The structures of all synthesized epoxy as well as vinyl ester resins are supported by their IR analyses results and further confirm using NMR spectral studies. Curing and decomposition behaviour of the resultant resins were analyzed by using DSC and TGA. Thermogravimetric results revealed that resultant vinyl ester resins have good thermal stability.

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